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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Stereospecific Copolymers of Styrene and Butadiene

5 We, TEXAS-U.S. CHEMICAL COMPANY, a corporation of the State of Delaware, United States of America, having its principal office at Port Neches, Texas, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to stereospecific copolymers of styrene and butadiene.

15 The literature dealing with butadiene polymers, styrene polymers and copolymers thereof is quite extensive. Recently there has been substantial attention given to the preparation of butadiene polymers of substantially all cis orientation. The cis orientation of the butadiene unit in the butadiene polymer composition gives extraordinary properties of toughness to the polymer and, in fact, has introduced certain new problems in the milling of the butadiene material answering this description.

25 Butadiene and styrene monomers have very different polymerization reactivities. Consequently the preparation of controlled structure copolymers is difficult. It has not hitherto been possible to produce solution copolymers without the substantial loss of stereo regularity of cis 1,4 content, in the butadiene portion of the molecule.

35 The present invention provides a substantially linear, styrene-butadiene copolymer of substantially random configuration having a styrene content of from 2% to 55%, by weight, wherein at least 90% of the butadiene units are in cis-1,4 configuration, said copolymer having an intrinsic viscosity, measured in toluene, of from 1 to 4.

40 Thus, the present invention provides tough copolymers of styrene and butadiene containing controlled amounts of styrene. At least 90% of the butadiene units in the polymer molecule are in the cis -1,4 configuration, with

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the remainder of the butadiene units being in vinyl (1,2) or trans -1,4 configuration. The copolymers contain between 2% and 55% by weight styrene, with the remainder essentially butadiene.

50 The copolymers of butadiene and styrene of this invention are copolymerized under solution conditions, the process being characterized by the fact that ether is not present in the polymerization reaction mixture either in the catalyst or the solvent. The butadiene and styrene are copolymerized by contacting a mixture of the monomers with a catalyst consisting of an ether-free organomagnesium compound and a titanium tetrahalide compound in which the titanium is maintained in the tetravalent state.

75 Thus the invention provides a process for the preparation of butadiene-styrene copolymers containing from 2% of styrene to 55% by weight of styrene, said copolymers being characterized by the cis-1,4 configuration of at least 90% of the butadiene units in the polymer molecules, the process comprising contacting a butadiene and styrene mixture under solution conditions with an iodine-containing catalyst comprising (i) at least one ether-free organomagnesium compound corresponding to the formula $RMgX$ or R_2Mg , wherein X is chlorine iodine, bromine or fluorine and R is a hydrocarbyl radical containing 1—30 carbon atoms, and (ii) a titanium tetrahalide, the catalyst containing iodine in the elemental state or as a halide constituent of catalyst component (i) or (ii), the amount of said catalyst being 0.0001 mol to 0.01 mol of catalyst per mol of butadiene in the reaction mixture, inducing polymerization at a temperature in the range from $-10^{\circ}C$ to $150^{\circ}C$, stopping polymerization and recovering polymers, the polymerization mixture being substantially free from ethers. Preferably the catalyst is substantially free from titanium in any valency state other than the tetravalent state.

The copolymer of butadiene and styrene of the invention containing from about 2% to about 55% by weight styrene, share the common characteristics of being physically tough materials and structurally having at least 90% of the butadiene units in the cis configuration and of being essentially linear materials as indicated by the absence of gel (a property related to severe branching and cross-linking). The properties of these copolymers vary with the styrene content: relatively low styrene copolymers, i.e., those having from 2% to 25% of styrene are elastomeric materials; the high styrene copolymers, i.e., those containing from 25% to 55% styrene are tough solid generally resembling soft thermoplastic solids. The copolymer has uniformly reproducible properties and characteristics when produced under the specified conditions. The copolymers of the invention are of substantially random configuration i.e. a configuration wherein monomeric styrene and butadiene moieties are randomly interspersed along the polymer chain.

The low styrene copolymers possess excellent processing characteristics and readily blend with conventional elastomer compounding ingredients, when mixed in a Banbury mixer or on rubber mills. The physical properties of these materials are characteristic of elastomeric copolymers, but the heat build-up property is lower. The butadiene-styrene copolymers of this invention preferably contain at least 5% of styrene to appreciably modify the characteristics which are exhibited by cis-1,4-polybutadiene. The low styrene copolymers of this invention have Mooney viscosities (ML-4 at 212°F) ranging from 5 to values in excess of 100. Those having Mooney viscosities of between 10 and 100 are preferred for use as elastomeric materials. The copolymers of the invention have an intrinsic viscosity $[\eta]$ when measured in toluene solution of between 1 and 4.

The styrene-butadiene copolymers of this invention are obtained by polymerizing in solution with the catalyst defined above whose use in the formation of cis-polybutadiene forms the subject matter of our United States patent specification No. 3,424,736.

The organomagnesium compounds used in preparing the polymers of this invention have the general formulas $RMgX$, R_2Mg , or mixtures thereof, wherein X is chlorine, iodine, bromine or fluorine, and R is an hydrocarbyl radical containing 1—30 carbon atoms. The titanium tetrahalide component is represented by the general formula TiX_4 , wherein X is defined as in the organomagnesium compound but may represent the same or combinations of different halogen atoms.

The ether-free organomagnesium compounds usable in the catalyst system of this process are exemplified by the following: dodecyl magnesium iodide, dodecyl magnesium

bromide, decyl magnesium iodide, stearyl magnesium iodide, ethyl magnesium iodide, methyl magnesium iodide, methyl magnesium chloride, myristyl magnesium bromide, nonyl magnesium iodide, nonyl magnesium fluoride, naphthyl magnesium bromide, phenyl magnesium bromide, phenyl magnesium chloride, ethyl magnesium chloride, hexyl magnesium iodide, 2-ethylhexyl magnesium bromide, methyl cyclohexyl magnesium iodide, p-tertiary butyl benzyl magnesium iodide, hexadecyl magnesium chloride, cetyl magnesium fluoride, didodecyl magnesium, didecyl magnesium, distearyl magnesium, diethyl magnesium, dimethyl magnesium, dimyristyl magnesium, dinonyl magnesium, dinaphthylmagnesium, diphenyl magnesium, dihexyl magnesium, di-2-ethylhexyl magnesium, dimethylcyclohexyl magnesium, di-p-tertiary butyl benzyl magnesium, dihexadecyl magnesium and dicetyl magnesium.

The titanium tetrahalide of the catalyst system employed in this invention is exemplified by the following: titanium tetraiodide, titanium tetrabromide, titanium tetrachloride, titanium tetrafluoride and mixed titanium tetrahalides such as titanium dichloride diiodide, titanium dibromide diiodide and titanium monobromide triiodide.

A preferred catalyst is one in which the titanium tetrahalide is titanium tetraiodide and the organomagnesium compound is an aliphatic or aryl hydrocarbyl magnesium compound in which the hydrocarbyl radical contains 6 to 24 carbon atoms.

The ether-free organomagnesium compound-titanium tetrahalide catalyst preferably comprises 1.0 to 10 (and more preferably 2 to 5, equivalents of organomagnesium compound per mol of titanium tetrahalide. The concentrations of catalyst employed in the production of the styrene-butadiene copolymers are best expressed in mols of catalyst, that is, equivalents of organomagnesium compound plus mols of titanium tetrahalide, per mol of butadiene reactant. (Under this formula 1 mol of catalyst = $1/2$ equivalent organomagnesium compound + $1/2$ mol titanium tetrahalide). The broad catalyst concentration range is between 0.00001 and 0.01 mol of catalyst per mol of butadiene in the reaction mixture. The preferred catalyst concentration is between 0.00007 mol and 0.0045 mol of catalyst per mol of butadiene reactant.

Because of impurities in the solvents, monomers, and catalyst components, it is desirable to maintain close control over the polymerization reaction in order to obtain the desired polymer. By nature, these solution polymerization reactions are very sensitive, and a considerable amount of manipulation, experimentation, trial and error are necessary in order to achieve the desired results.

The ratio of styrene to butadiene in the starting mixture is not the sole factor in

determining the styrene/butadiene ratio in the product. Accordingly, it is necessary to control the process variables generally in order to ensure that the product contains between 2% and 55% by weight of styrene; such control is within the skill of the man skilled in the art, trial and error methods being applicable if required.

A requirement of the ether-free organo-magnesium-titanium tetrahalide catalyst system, in order to obtain a copolymer having a high cis-1,4 content, is that iodine is present in the catalyst system either as elemental iodine or a substituent of the organo-magnesium compound or of the titanium tetrahalide. The presence of the iodine in the catalyst system seems to exert a directing influence on the polymerization reaction, as it does when used in the preparation of cis-1,4-polybutadiene, with the result that the butadiene component of the copolymer of the invention has a cis-1,4 content of at least 90%.

As disclosed in the afore-identified U.S. Patent No. 3,424,736, the ether-free organo-magnesium-titanium tetrahalide catalyst system can be prepared in a number of ways.

1. The catalyst components can be pre-mixed and maintained at a temperature below 0°C prior to their addition to the polymerization reaction mixture;

2. They can be pre-mixed in a concentrated slurry in an inert hydrocarbon solvent wherein the catalyst concentration is at least 10 and preferably more than 50 weight percent.

3. The components can also be pre-mixed at lower concentration levels and at higher temperatures, in which case the titanium is reduced in valence from 4 to 3, as is well annotated in the chemical literature. In this case, the titanium may be restored to the active tetravalent state while in the reaction mixture by the addition of an oxidizing agent, such as iodine, oxygen, or organic solvent soluble oxidants.

The preferred procedure for preparing the active ether-free organomagnesium-titanium tetrahalide catalyst system involves formation of the catalyst "in situ" in the reaction by the separate addition of the individual catalyst components, that is, the ether-free organo-magnesium compound and the titanium tetrahalide, to the reaction mixture containing styrene and butadiene. In this manner, the conversion of the active catalyst to an inactive reduced state is substantially eliminated as discussed in the abovementioned United States patent specification No. 3,424,736.

Both the styrene and butadiene reactants should be relatively free of moisture, preferably below 10 parts per million. The reactants should also be essentially free from sulfur, carbonyl groups, and peroxides. Such monomeric materials can be prepared in the manner disclosed in U.S. Patent 3,260,766. In addition

the monomers can be freed of inhibitors by passing them through an alumina bed prior to adding them to the polymerization reaction.

The polymerization process of the invention is effected at temperatures from -10°C to 150°C with temperatures between -10°C and 90°C being preferred. Contact of the butadiene and styrene with the catalyst is preferably effected at a temperature between 0°C and 50°C. Because of the stability and temperature insensitivity of the catalyst system employed in this process, it is not necessary to maintain rigid control over temperature during the polymerization. In fact, the reaction can be allowed to exotherm adiabatically, in which case the heat liberated augments the rate of reaction. The polymerization process is usually effected at pressures sufficient to maintain a liquid phase operation. Broadly speaking, pressures between atmospheric and 500 psig (pounds per square inch gauge) may be employed; but pressures between 30 and 100 psig are usually adequate to maintain the liquid phase operation.

The copolymerization reaction is usually effected in the presence of an inert hydrocarbon solvent. Aromatic hydrocarbons such as benzene, toluene or xylene are preferred. Cyclohexane is of particular interest in this particular copolymerization, as it can be used as an auxiliary aid in controlling the polymerization. The solvents must be dry and free from any significant sulfur or peroxide content.

The copolymerization reaction can be effected batchwise or in a continuous manner. The usual reaction time for the polymerizations contemplated in this invention can vary from 1/4 hour to 20 or more hours with the reaction temperature, the catalyst activity, the solvent, and the size of the polymerization reaction mixture all affecting the duration of the reaction.

Various procedures may be employed for the isolation of the copolymer. For example, it can be precipitated from the hydrocarbon solution by the addition of a low molecular weight alcohol, such as methanol or ethanol. A more common industrial procedure involves the precipitation of the copolymer in the form of a crumb by steam floccing. A third alternative involves conversion of the copolymer to a latex by the addition of water and emulsifying agent and the precipitation of the latex by well-known precipitation technique.

The preparation and properties of the styrene butadiene copolymers of this invention is further illustrated in the following examples, in which all parts and percentages are by weight unless noted otherwise and all the products have an intrinsic viscosity, measured in toluene, of from 1 to 4. All reported percentages of "cis," "trans" and "vinyl" are based on the butadiene portion of the copolymer.

EXAMPLE I

This example demonstrates the preparation of styrene butadiene copolymer containing 5% bound styrene. The example also illustrates the fractionation of the polymer produced and the uniformity of styrene incorporation.

The polymerization was conducted in a glass bottle tested to withstand internal pressures of 100 psig. The bottle was carefully cleaned, dried and swept free of air by a stream of dry inert gas such as argon. The bottle was sealed with a self-sealing rubber liner and a metal crown cap through which ingredients could be added or withdrawn by means of a hypodermic needle and syringe. To this glass bottle was added 24 grams of styrene and 12 grams of butadiene. To this solution was added 0.45 milliequivalent of do-

decyl magnesium bromide suspended in dry xylene followed by 0.15 millimol of titanium tetraiodide dissolved in dry benzene. The polymerization reaction was shortstopped by the addition of methanol after two hours. The polymer was precipitated by alcohol and dried.

Analysis of the product by infrared spectroscopy showed it to contain 5% bound styrene and to have a cis content of the butadiene portion in excess of 90%. The dried polymer was an elastic material. 4-1/2 grams of this polymer were dissolved in 100 milliliters of benzene, 10 ml of the clear benzene solution were added to varying quantities of isopropyl alcohol and the precipitated polymer was washed, dried and analyzed for cis, trans and vinyl content and % bound styrene, as follows:

Sample	Isopropyl Alcohol (ml)	Polymer Recovered	Cis	Trans	Vinyl	Styrene
1	6	0.03	95.2	1.3	3.5	5
2	7	0.29	96.0	1.5	2.5	5
3	8	0.36	96.0	1.5	2.5	5
4	9	0.37	96.0	1.4	2.6	5
5	10	0.37	95.9	1.5	2.6	5

The fractions shown are almost identical, indicating that the structure of the product is uniform. The constancy of bound styrene contents of the several fractions establishes that the product is a true copolymer and not a mixture of polybutadiene and polystyrene.

EXAMPLE II

This example demonstrates the preparation of the styrene-butadiene copolymers having various quantities of bound styrene incorpo-

rated into the chain. The following reactions were conducted in glass bottles, as described in Example I, in which the materials shown in the table were charged in the order listed. The organomagnesium compound and the titanium tetraiodide were added separately as solutions in benzene in accordance with the procedure of Example I. The dried products were all elastic substances. The structure of the products was determined by infrared measurements.

Benzene (grams)	83.6	79.2	70.4	52.8	35.2	17.6
Butadiene (grams)	12	12	12	12	12	12
Styrene (grams)	4.4	8.8	17.6	35.2	52.8	70.4
Diphenylmagnesium (meq)	0.6	0.6	0.6	0.6	0.6	0.6
Titanium tetraiodide (mM.) (mM is millimole)	0.2	0.2	0.2	0.2	0.2	0.2
Yield	10.9	10.3	10.8	11.0	11.2	11.5
% Conversion (Based on Butadiene)	90.9	85.8	90.0	91.7	93.4	95.9
Analysis of polymer						
% Styrene	9.2	9.7	10.8	12.4	14.7	17.4
% Cis	96.6	96.3	96.5	96.5	96.6	96.6
% Trans	1.1	1.2	1.1	1.1	1.1	1.1
% Vinyl	2.3	2.5	2.4	2.4	2.3	2.3

EXAMPLE III

5 A series of experiments similar to Example II were conducted in glass bottles with the results reported in the table. The phenyl magnesium compound used was in an ether-free benzene solution of a mixture of diphenyl-

magnesium and phenylmagnesium chloride in the approximate mole ratio of 3:1, referred to hereinafter as "phenylmagnesium compound." 10

The pertinent data for these experiments are also shown in the table.

Benzene (grams)	82	72.8	54.8	36.4	18.2
Butadiene (grams)	9	9	9	9	9
Styrene (grams)	9.0	18.2	36.2	54.6	72.8
Phenylmagnesium Compound (meq)	0.45	0.45	0.45	0.45	0.45
Titanium tetraiodide (mM)	0.15	0.15	0.15	0.15	0.15
Yield	8.5	8.8	8.3	9.0	9.1
% Conversion (Based on Butadiene)	94.4	97.7	92.1	100.0	101.0
Analysis of polymer					
% Styrene	8.7	9.7	9.8	14.9	18.1
% Cis	96.6	96.8	96.8	96.9	97.0
% Trans	1.2	1.1	1.1	1.2	1.1
% Vinyl	1.2	2.1	2.1	1.9	1.9

After initiation at 50°C the polymerizations were allowed to exotherm from 50°C. for 30 minutes after which they were coagulated by the addition of methyl alcohol. One part of a stabilizer was added to the coagulant

based on 100 parts of estimated dry polymer, and the product was dried for 18 hours at 60°C. and 30" of mercury. The isolated polymeric products were all elastic.

EXAMPLE IV

A series of bottle runs were conducted using the recipes shown in the Table.

Benzene (grams)	92.0	89.3	84.7	75.2	56.6	37.6	18.8
Butadiene (grams)	6	6	6	6	6	6	6
Styrene (grams)	2.0	4.7	9.3	18.8	37.4	56.4	75.2
Phenylmagnesium Compound (meq)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Titanium tetraiodide (mM)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Yield (grams)	3.0	2.2	4.2	3.8	4.0	5.5	5.0
% Conversion	50.0	36.7	70.1	63.5	66.8	91.9	83.5
Analysis of Polymer							
% Styrene	8.5	8.9	9.0	8.8	10.9	17.2	19.2
% Cis	96.5	96.9	96.8	97.0	97.0	97.1	97.0
% Trans	1.3	1.1	1.2	1.1	1.1	1.2	1.2
% Vinyl	2.2	2.0	2.0	1.9	1.9	1.7	1.8

The polymerization reactions were run for 5 hours, following which 5 ml. of 6% di-methyl amine in isopropanol containing 0.1 gram of 2,6-di-t-butyl-p-cresol were added to terminate the reaction. The polymers were separated from the solution by adding methyl alcohol and the products were dried as described in Example III. The dried products were all elastic substances.

EXAMPLE V

Two one gallon reactor size experiments were run simultaneously. The two experiments were designated A and B. The butadiene, benzene and styrene used in these runs were deaerated and then passed through an activated alumina column.

The materials were charged into the reactors in the proportion shown in the table. The components of the catalyst dissolved in benzene were added separately after all the other ingredients had been charged.

20

25

30

	A	B
Benzene (grams)	856	819
Butadiene (grams)	256	255
Styrene (grams)	1604	1603
Phenylmagnesium Compound (meq)	13.2	13.2
Titanium tetraiodide (mM)	4.4	4.4
% Conversion (based on butadiene)	85 (approximate)	85 (approximate)
Analysis of Polymers		
% Styrene	10.3	10.4
% Cis	96.5	96.4
% Trans	1.2	1.2
% Vinyl	2.3	2.4

The reaction in both cases were initiated at 15°C. The pressure in reactor A was 50 psig and the pressure in reactor B was 55 psig. In both cases the reaction immediately exothermed, and by applying full cooling, the reaction temperature was maintained at 24°C. Both reactions were shortstopped and coagulated after 16-1/2 hours by adding a solution of 200 ml of 9% dimethylamine in benzene, 3 grams of a phenolic stabilizer and 30 ml of methanol. The polymer was separated from the solvent by adding 5 gallons of methanol, following which it was dried at 60°C. and 30" mercury. The data for the analytical figures shown were all obtained by infrared analysis. The final product in both cases was an elastomer which had a Mooney viscosity (ML-4, @ 212°F.) of 10.

EXAMPLE VI

The process followed in the preceding examples was scaled up to 10 gallons. In contrast to Example V, however, the reaction was allowed to exotherm from 25°C. after the initiation, and no effort was made to control the temperature of polymerization.

A 10 gallon reactor was charged with 23.5 lbs. of dry benzene, 5.8 lbs. of butadiene, 35.3 lbs. of styrene. All ingredients were pretreated in the same manner as in Example V. A solution of phenylmagnesium compound, containing 115.5 milliequivalents of organomagnesium dissolved in benzene and 1755

grams of titanium tetraiodide (38.5 millimoles) also dissolved in benzene, were added separately to the reaction mixture. The reaction was run for 403 minutes (6.7 hours) after which the polymerization was shortstopped with a solution of 2 liters of 9% dimethylamine in benzene, 30 grams of a phenolic stabilizer and 200 cc. of methanol. The polymer was separated from the solution by steam stripping and the product was dried at 60°C. and 30" of mercury for 18 hours. A total of 1050 grams of an elastic polymer was obtained, having a Mooney viscosity (ML-4, @ 212°F.) of 16. Infrared analysis of the final product showed it to contain 10% styrene, and 92.5% cis, 2.4% trans and 5.1% vinyl in the butadiene portion of the polymer.

The copolymer obtained from this polymerization was compounded on a rubber mill with the following ingredients in the proportion shown: polymer—100 parts, easy processing channel black—40 parts, zinc oxide—5 parts, sulfur—2 parts, stearic acid—2 parts, and benzthiazyl disulfide—3 parts.

The polymer banded easily on the mill rolls at 105°F. and the compounding ingredients were added without any difficulty. Mixing was continued until the compound was smooth and the compounding ingredients were homogeneously dispersed in the polymer. The compound was cured at 292°F. In accordance with ASTM procedure, the cured slabs were tested with the following results:

Time of Cure	Tensile Strength (PSI)	Stress @ 300% Elong. (PSI)	Elongation %
25 min.	1375	290	1200
50 min.	2100	300	1200
100 min.	2190	390	1070

EXAMPLE VII

Two simultaneous 1 gallon reactor (A & B) experiments were carried out following the procedure of Example V except that no tem-

perature control was maintained after initiation. The reactors were charged as noted in the table.

	A	B
Benzene (grams)	843	843
Butadiene (grams)	260	260
Styrene (grams)	1599	1601
Phenylmagnesium compound (meq)	11.55	11.55
Titanium tetraiodide (mM)	3.9	3.9
Initiation temperature	24°C.	26°C.
Maximum temperature	64°C.	58°C.
Initiation pressure	35 psig	40 psig
Maximum pressure	40 psig	44 psig
Time of reaction	19 hrs.	18.5 hrs.
Yield (grams)	275.3	271.2

Analysis of Polymers	A	B
% Styrene	19.3	16.9
% Cis	96.5	96.5
% Trans	1.1	1.1
% Vinyl	2.4	2.4
Mooney viscosity (ML—4, @ 212°F.)	17.5	12.0

15 The polymerization reactions were terminated by pouring the reaction mixture into one gallon containers in which a solution of 200 ml of 9% dimethylamine in benzene, 3 grams of 2,6-di-t-butyl-p-cresol and 30 cc. of methanol had been charged. Both solutions were coagulated in 10 gallons of methyl alcohol. The polymer was vacuum dried at 60°C. and 30" of mercury for 24 hours.

20 The dried, gel-free, elastic polymeric products from this example were combined and compounded on a rubber mill in the same manner as Example VI and using the same vulcanizate recipe and procedure. The physical properties for the compounds follow: 25

Time of Cure	Tensile Strength (PSI)	Stress @ 300% Elongation (PSI)	Elongation %
25 min.	1750	610	790
50 min.	1800	1075	500
100 min.	1850	1210	420

EXAMPLES VIII TO XI

These examples were run in accordance with the procedure shown in Example VI.

5 The polymerization ingredients were pre-treated in the same manner as in the preceding

examples and charged into a 10 gallon reactor. The quantities of materials and order of addition used in each of the reactions are shown in the table.

10

Example No.	VIII	IX	X	XI
Benzene (lbs.)	23.5	23.5	20.6	20.6
Butadiene (lbs.)	5.8	5.8	5.7	5.7
Styrene (lbs.)	35.3	35.3	35.3	35.3
Phenylmagnesium Compound (meq)	115.5	82.5	66	57.75
Titanium tetraiodide (mM)	38.5	27.5	22	19.25
Initiation temperature	50°C	50°C	50°C	50°C
Maximum temperature	65°C>	75°C	75°C>	75°C
Initiation pressure (psig)	40	40	40	40
Time of reaction (hours)	6½	23½	20.5	23½
Yield (grams)	2303	2450	2100	2525
% Gel	0	0	0	0
[η] Intrinsic viscosity	—	1.53	2.16	2.13
Analysis of Polymers				
% Styrene	10.3	7.7	9.3	7.8
% Cis	95.6	93.5	93.5	95.1
% Trans	1.4	1.9	1.7	1.8
% Vinyl	3.0	4.6	4.8	3.1
Mooney viscosity (ML—4, @ 212°F.)	17.5	15	33	36.5

15 The polymers from Examples VIII, IX, X and XI which were all gel-free elastic solids, were compounded in accordance with the recipe and procedure of Example VI. The

polymers exhibited the same excellent processing characteristics and when tested according to the ASTM procedures yielded the following physical property values:

Sample	Tensile (PSI)			Stress @ 300% Elongation (PSI)			Elongation %		
	25'	50'	100'	25'	50'	100'	25'	50'	100'
VIII	2330	2150	2125	325	450	525	1200	930	800
IX	1920	2150	2150	500	530	700	1150	840	700
X	2570	2190	2130	400	650	800	1090	720	610
XI	2400	2300	2225	325	500	600	1060	800	700

EXAMPLE XII

A non-elastic styrene-butadiene copolymer containing a large amount of bound styrene was prepared. A one gallon reactor experi-

ment was conducted following the procedure of Example VII. The afore-listed materials were charged with the reported results:

Benzene (grams)	918
Butadiene (grams)	264
Styrene (grams)	1601
phenylmagnesium compound (meq.)	2.75
Titanium tetraiodide (mM)	2.75
Initiation Temp.	75°C.
Time of Reaction (Hours)	4.8
Yield (grams)	20
Analysis of Polymer	
% Styrene	53.4
% Cis	91.8
% Trans	5.7
% Vinyl	3.7

10 Polymerization was terminated as in Example VII, and the polymer isolated by alcohol coagulation. When dry, the product was not a typical elastic solid but had the appearance of a soft thermoplastic solid.

15 A sample of this polymer was subjected to quantitative ozonolysis to yield a very low molecular weight residue which was isolated after alkaline treatment of the hydrolyzed ozonolysis product. This indicated the presence

of some very low molecular weight polystyrene blocks in the copolymer. 20

EXAMPLE XIII

A styrene-butadiene copolymer having high bound styrene was prepared in a ten gallon reactor following the procedure of Example VI, except that a higher temperature and lower catalyst level were employed as well as a different Mg/Ti ratio as reported in the table: 25

Benzene (lbs.)	23.5
Butadiene (lbs.)	5.8
Styrene (lbs.)	35.3
Phenylmagnesium compound (meq.)	28.9
Titanium tetraiodide (mM)	19.25
Initiation temperature	55°C.
Polymerization temperature	75°C.
Time of Reaction (Hours)	22.75
Yield (grams)	475
Analysis of Polymer	
% Styrene	47.3
% Cis	92.0
% Trans	4.8
% Vinyl	3.2

5 The polymerization was shortstopped and the polymer isolated and dried as in Example VI. The dried polymer was not a typical elastic solid but resembled a soft thermoplastic solid.

10 A sample was subjected to quantitative ozonolysis and hydrolysis. There was no alkaline insoluble material remaining from the hydrolyzed ozonolysis product. This establishes that even at very high bound styrene content level these butadiene-styrene copolymers are random. Furthermore, it establishes that poly-

styrene is not produced during the reaction.

EXAMPLE XIV

15 The effect of incrementally adding the catalyst to determine the feasibility of increasing the molecular weight was tested. Glass bottles were charged according to the recipe in the table, with 1/2 the total amount of catalyst 20 shown. The reactants were allowed to polymerize at 70°C., and the remainder of the catalyst was added at the time indicated.

	1	2	3
Benzene (grams)	82.1	86	93.4
Butadiene (grams)	6	6	6.1
Styrene (grams)	6	6	6
Phenylmagnesium compound (meq)	0.25	0.25	0.25
Titanium tetraiodide (mM)	0.10	0.10	0.10
Time of second catalyst addition (minutes)	45	90	135
Total time of reaction (hours)	12	12	12
Yield (grams)	6	6	6
Analysis of Polymers			
% Styrene	10.0	11.5	10.0
% Cis	93.9	92.7	93.2
% Trans	1.7	1.9	1.8
% Vinyl	3.75	4.65	4.35
$[\eta]$ Intrinsic Viscosity	1.58	2.35	2.14

5 The polymerizations were shortstopped with methanol, and a small amount of phenolic stabilizer was added. The polymer was separated from the solvent by alcohol addition and dried in the usual manner. Inspection of the final product revealed that the three samples had higher molecular weights than those obtained in control experiments in accordance with the preceding examples.

EXAMPLE XV

Both monomers, butadiene and styrene, were added incrementally to the reaction mixture to determine the feasibility of raising the molecular weight in this manner. Glass bottles were charged in the same manner as in the preceding examples, and after initiation at room temperature were allowed to polymerize at 70°C. The full amount of catalyst was used, but only 1/2 of the total butadiene and styrene was charged. The remainder of monomers was added at the time indicated.

Sample No.	1	2
Benzene (grams)	87.7	89.0
Butadiene (grams)	6	6
Styrene (grams)	6	6
Phenylmagnesium compound (meq.)	0.5	0.5
Titanium tetraiodide (mM)	0.20	0.20
Time of second monomer addition (minutes)	45	90
Total time of polymerization	12 hrs.	12 hrs.
Yield (grams)	5.7	4.5
Analysis of Polymers		
% Styrene	6.8	5.6
% Cis	92.6	92.2
% Trans	1.9	2.4
% Vinyl	5.5	5.4
[η] Intrinsic viscosity	1.89	2.09

Each of the polymerizations was coagulated and dried in the same manner as in the preceding example.

5

EXAMPLE XVI

Polymerizations were conducted in glass bottles, comparing the effects of cyclohexane

and benzene as the solvent using the recipe shown in the table. The reactions were initiated at room temperatures and polymerized overnight at 70°C. The polymerization was shortstopped and the product polymer finished in the same manner as the preceding examples.

10

	1	2	3
Cyclohexane (grams)	73.8	77.7	
Benzene (grams)			88
Butadiene (grams)	6.1	6.0	6.4
Styrene (grams)	6	6	6
Phenylmagnesium compound (meq)	0.5	0.5	0.5
Titanium tetraiodide (mM)	0.2	0.2	0.2
Yield (grams)	5.5	5.4	6.9
Analysis of Polymers			
% Styrene	5.7	5.2	11.2
% Cis	90.64	90.75	94.39
% Trans	3.16	3.02	1.61
% Vinyl	6.20	6.23	4.00

EXAMPLE XVII

A high molecular weight copolymer of butadiene and styrene was obtained following the

procedure of Example VI, except that the order of charging and amounts noted in the following table were used. 5

Benzene (lbs.)	23.5
Styrene (lbs.)	35.3
Butadiene (lbs.)	5.8
Titanium tetraiodide (mM)	17.52
Phenylmagnesium compound (meq)	57.75
Initiation Temperature	50°C.
Maximum temperature	>75°C.
Time of Reaction (hours)	4.0
Yield (grams)	1910
% Gel	0
Intrinsic viscosity	3.52
Analysis of Polymer	
% Styrene	8.3
% Cis	93.6
% Trans	1.8
% Vinyl	4.6

10 The polymer was isolated by steam stripping and flocculation. It was a highly elastic solid having a Mooney viscosity (ML-4 @ 212°F.) greater than 100. It showed evidence of severe slippage in the Mooney Viscometer

during testing. It was tested for vulcanizate properties by compounding with oil and carbon black in a Banbury mixer according to the following recipe: 15

	Parts
Polymer	100
Highly Aromatic Oil	50
HAF Carbon Black	75
Zinc Oxide	4.5
Resin 731—D (disproportionated rosin acid)	7.5
Stearic Acid	3.0
Antioxidant	1.5

5 This oil-extended, carbon black masterbatch had a compound Mooney Viscosity (ML-4 @ 212°F.) of 47. The following curatives (based on 100 parts of elastomer) were added to the masterbatch on a cool 6" X 12" rubber mill:

Highly Aromatic Oil	7.50
Sulfur	2.62
Nobs No. 1 *	1.36

* American Cyanamid trademark for a 90:10 mixture of N-oxydiethyl benzthiazole-2-sulfonamide and benzthiazyl disulfide. 10

When fully compounded the mix was milled at 260°F. for 2 minutes and prepared for vulcanization. The compound was vulcanized at 292 F. In accordance with ASTM procedures, the vulcanized material was tested with the following results: 15

Time of Cure	Tensile Strength (PSI)	Stress @ 300% Elong. (PSI)	Elongation %	Goodrich HBU @ 100°F. (°F)
25 min.	2475	700	800	60
50 min.	2475	975	630	51
100 min.	2425	1000	600	48

20 This oil-extended, high cis content butadiene-styrene copolymer showed high tensile strength and low heat build-up (HBU).

EXAMPLES XVIII—XIX

Two reruns following the procedure of Example VI were conducted in a 10 gallon reactor. Only the times of reaction and amounts were varied, as noted in the following table. 25

Example No.	XVIII	XIX
Benzene (lbs.)	23.5	23.5
Butadiene (lbs.)	5.8	5.8
Styrene (lbs.)	35.3	35.3
Phenylmagnesium Compound (meq)	57.75	57.75
Titanium tetraiodide (mM)	19.25	19.25
Initiation temperature	50°C.	50°C.
Maximum temperature	75°C.	75°C.
Time of reaction (hours)	16	1
% Gel	0	0
Intrinsic Viscosity [η]	2.21	1.96
Analysis of Polymers		
% Styrene	8.8	2.6
% Cis	93.4	93.5
% Trans	2.0	1.7
% Vinyl	4.6	4.8
ML-4 @ 212°F.	24	24

These polymers were shortstopped in accordance with the procedure of Example VI and isolated by steamstripping. The isolated polymer products were elastic solids.

EXAMPLE XX

The vulcanizate properties of the high cis content butadiene-styrene copolymer products of specified examples herein were obtained on materials compounded in a Banbury mixer using the following recipe and procedure:

Polymer	100
HAF Carbon	50
Zinc Oxide	3
Disproportionated rosin acid (Resin 731-D)	5
Stearic Acid	2
Antioxidant	1
Highly Aromatic Oil	5
Sulfur	2
Nobs No. 1	0.9

15 The Banbury mixer was run at 100 RPM and an initial temperature of 120°F. Polymer was added, the ram lowered and mixed for 1 minute. After this, one-half of the black and zinc oxide were added and mixed for 2 minutes. Then the second half of the black, rosin acid, stearic acid, and antioxidant were added and mixed for 3 minutes. At the end of this
20 mixing procedure the masterbatch was removed from the Banbury, usually at a temperature of 275—300°F. The masterbatch at this point generally consisted of one or two large, shiny lumps with no loose (undispersed)

black present. The masterbatch was sheeted on a cool 6" × 12" mill and a sample removed for determination of the compound Mooney viscosity (ML-4 @ 212°F.) The oil and curatives were added on the mill at 120°F. The mill temperature was then raised to 260°F. and the compound milled for two minutes at this temperature. The hot compound was cut from the mill and sheeted on a cool mill. Vulcanization was accomplished at 292°F. The vulcanizate properties are listed in the following table:

Example No.		VIII	IX	X	XI	XVIII	XIX
% Styrene		10.3	7.7	9.3	7.8	8.8	2.6
ML-4 @ 212°F.		17.5	15	33	36.5	24	24
Compound ML-4		37	33.5	55.5	62	53.5	51
Tensile	25'	1675	1525	2350	2550	2400	2450
(PSI)	50'	2425	2200	2525	2650	2300	2400
	100'	2400	2250	2550	2725	2325	2250
S-300	25'	325	300	675	725	775	775
(PSI)	50'	575	725	1100	975	1075	1100
	100'	625	875	1300	1050	1125	1275
Elongation	25'	980	950	800	740	710	700
(%)	50'	880	750	550	620	550	510
	100'	760	630	510	570	380	460
Tensile @ 212°F. (PSI)	50'	1280	1250	1330	1430	1230	1240
% Retention of Tensile		52.8	56.8	52.7	53.9	53.5	51.7
Goodrich	25'	—	—	84	85	69	62
HBU @ 100°F.	50'	82	84	62	66	60	58
(°F.)	100'	82	80	60	66	59	51

These properties indicate that the butadiene-styrene copolymers of this invention have useful applications in tire manufacture and other rubber product uses. They possess excellent tensile strength, which is retained to the extent of about 52%—56% at elevated temperatures.

The specific catalysts, solvents, reagents and reaction conditions exemplified are illustrative of all those disclosed to be operative. Other catalysts, solvents, reagents and reaction conditions within the scope of the disclosure may be selected and used in accordance with the disclosure, to produce the styrene-butadiene copolymers of the present invention.

The low styrene copolymers are useful tough elastomers and may be used for example to manufacture tires, tubing, and packing. The high styrene copolymers may be used to manufacture tire liners, floor tiles, and high impact strength plastics.

WHAT WE CLAIM IS:—

1. A substantially linear, styrene-butadiene copolymer of substantially random configura-

tion having a styrene content of from 2% to 55%, by weight, wherein at least 90% of the butadiene units are in cis-1,4 configuration, said copolymer having an intrinsic viscosity, measured in toluene, of from 1 to 4.

2. The copolymer of claim 1 containing between 2% and 25% styrene, and being a tough elastomeric material having a Mooney viscosity (ML-4 at 212°F) of between 10 and 100.

3. The copolymer of claim 2 containing between 5% and 25% styrene.

4. The copolymer of claim 1 containing between 25% and 55% styrene.

5. A process for the preparation of butadiene-styrene copolymers containing from 2% of styrene to 55% of styrene, said copolymers being characterized by the cis-1,4 configuration of at least 90% of the butadiene units in the polymer molecules, the process comprising contacting a butadiene and styrene mixture under solution conditions with an iodine containing catalyst comprising (i) at least one ether-free organomagnesium com-

- 5 pound corresponding to a formula RMgX or R_2Mg , wherein X is chlorine, iodine, bromine or fluorine and R is a hydrocarbyl radical containing 1—30 carbon atoms, and (ii) a titanium tetrahalide, the catalyst containing iodine in the elemental state or as a halide constituent of catalyst component (i) or (ii), the amount of said catalyst being 0.00001 mol to 0.01 mol of catalyst per mol of butadiene in the reaction mixture, inducing polymerization at a temperature in the range from -10°C to 150°C , stopping polymerization and recovering polymers, the polymerization reaction mixture being substantially free from ethers.
- 10 6. The process of claim 5 wherein said catalyst is substantially free from titanium in any valency state other than the tetravalent state.
- 15 7. The process of claim 5 or 6 wherein a mixture of substantially anhydrous butadiene and styrene in an aromatic hydrocarbon solvent medium, said solvent medium being inert to polymerization, is contacted at a temperature between -10°C . and 90°C . with a polymerization catalyst comprising a titanium tetrahalide and an ether-free organomagnesium Grignard compound which contains 1—30 carbon atoms, and the halogen of said organomagnesium compound is bromine, iodine or chlorine, said catalyst comprising said organomagnesium compound and said titanium tetrahalide in an equivalent: mol ratio of 1:1 to 10:1.
- 20 8. The process of claim 7 wherein said catalyst is formed by the separate addition of the organomagnesium compound and titanium tetrahalide to the mixture of butadiene and styrene.
- 25 9. The process of claim 7 or 8. wherein contact of butadiene and styrene for polymerization with said catalyst is effected at a temperature between 0°C . and 50°C .
- 30 10. The process of any of claims 7 to 9 wherein the titanium tetrahalide is titanium tetraiodide and said organomagnesium compound is an aliphatic or aryl hydrocarbyl magnesium compound in which the hydrocarbyl radical contains 6 to 24 carbon atoms.
- 35 11. The process of any of claims 7 to 10 wherein said equivalent to mol ratio of said organomagnesium compound and said titanium tetrahalide is between 2:1 and 5:1.
- 40 12. The process of any of claims 7 to 11 wherein said organomagnesium compound is a mixture of a dihydrocarbylmagnesium compound and a hydrocarbylmagnesium chloride.
- 45 13. The process of claim 12 wherein said organomagnesium compound is a mixture of diphenylmagnesium and phenylmagnesium chloride.
- 50 14. The process of any of claims 7 to 11 wherein said organomagnesium compound is diphenylmagnesium.
- 55 15. The process of any claims 7 to 11 wherein said organomagnesium compound is dodecylmagnesium bromide.
- 60 16. A process for the preparation of butadiene-styrene copolymers as in claim 5 substantially as herein described.
- 65 17. A process for the preparation of butadiene-styrene copolymers as in claim 5 substantially as described in any of Examples I to XIX.
- 70 18. Butadiene-styrene copolymers prepared by the process of any of claims 5 to 17.

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